

# CEMENT

AND

## CEMENT MANUFACTURE

PUBLISHED 20TH OF EACH MONTH.

PRICE 1/- A COPY.

ANNUAL SUBSCRIPTION 12s. POST FREE.

PUBLISHED BY  
CONCRETE PUBLICATIONS LIMITED,  
20, DARTMOUTH STREET, LONDON, S.W.1.  
TELEPHONE: WHITEHALL 4681.  
TELEGRAPHIC ADDRESS:  
CONCRETIUS, PARL, LONDON.

PUBLISHERS OF  
"CONCRETE & CONSTRUCTIONAL ENGINEERING"  
"CONCRETE BUILDING & CONCRETE PRODUCTS"  
"CEMENT & CEMENT MANUFACTURE"  
"THE CONCRETE YEAR BOOK"  
"CONCRETE SERIES" BOOKS, ETC.

VOLUME 7. NUMBER 2.

FEBRUARY 1934

### An Exit Temperature of 100°C. with the Wet Process.

By DIPL. ING. SCHIRM.

FOR some years endeavours have been made to achieve with the wet process of cement burning the same thorough exploitation of the exit gases as can be obtained with the dry process by means of the Lellep system. Up to a few years ago it was considered impossible to reduce the exit temperature to less than 400 deg. C., when working with a slurry of normal composition and 40 per cent. water content, without rendering the process uneconomic. Although it has been known for some time that considerably lower exit temperatures, and consequently reduced fuel consumption, can be achieved by lowering the output of the kiln, the results of operating in this manner have been by no means satisfactory. Apart from the fact that capital charges per ton of clinker are increased, the reduction in coal consumption is far from proportionate to the smaller heat losses in the exit gas. The reason for this is that lowering the output of the rotary kiln does not greatly reduce heat losses by radiation from the external surface of the kiln, so that these losses are increased for each ton of clinker produced, and balance to a large extent the savings made by reducing the temperature of the exit gas.

It is evident that data on rotary kiln exit temperatures must be interpreted with caution unless they are accompanied by information on the size and output of the kiln. The only real progress has been made by the use of chains. Exit temperatures as low as 250 deg. C. are said to have been achieved in this manner without any sacrifice of output. This is probably the most that can be gained by fitting chains in the back end of the rotary kiln, and then only when the slurry is of such a nature that a special type of chain can be used, which ensures a thorough wetting of even its hottest parts. It is proposed to examine the working conditions of a kiln with an exit temperature of about 100 deg. C. and then to discuss a few of the most modern types of kiln.

Calculation of the working conditions of such a kiln can only be approximate, and it is impossible to account for various losses due to the peculiarities of different types of kiln. But the results of these rough calculations are interesting, and it is possible to draw from them conclusions which give a good idea as to the suitability of new designs.

A kiln with an exit temperature of 100 deg. C. has been selected for investigation because this is the lowest temperature at which the water contained in the slurry can leave the kiln in the form of vapour. There are systems in which the water is removed from the raw material by mechanical means before the charge is fed into the kiln. This is done, for example, by filter presses which de-water the slurry to such an extent that it becomes paste-like or crumbly and can be handled in the same way as dry material in a Lellep installation. This case will not, however, be considered here, as most slurries do not lend themselves to this treatment.

The kiln with an exit temperature of 100 deg. C. is an ideal kiln, and in practice it will be necessary to reckon with a slightly higher gas temperature of, say, 120 deg. C., as is the case with the Lellep kiln, if it is to be certain that the entire water content of the raw material is carried off as vapour. The calculation will be restricted to the values that will suffice for the evaluation of new designs. Thus it will only be necessary to calculate fuel consumption and the volume and temperature of the gases entering the drying zone. A further simplification is obtained by assuming the fuel to consist of pure carbon. Comparative calculations based on the usual types of coal give such small differences that the simplified method is amply justified. Ten per cent. of excess air has been assumed throughout; and it will suffice for the present purpose to indicate the sense in which the various results will be influenced if a different excess of air be taken. Nevertheless, the differences caused by varying the excess of air are so considerable that it would be well worth while to analyse the influence of this variable.

There are various methods of designing the ideal kiln with an exit temperature of 100 deg. C.; in the present case the calculations are based upon the Lellep kiln. This makes for simplicity; and the accuracy achieved is sufficient for the purpose. A normal slurry with 40 per cent. water content is assumed, and the solid is taken to consist of 75 per cent. calcium carbonate and 25 per cent. clay. Thus 100 kg. clinker = 37.3 kg. clay + 112 kg.  $\text{CaCO}_3$  = 149.3 kg. dry raw material. In the Lellep dry process the average moisture content is 10 per cent. (16.7 kg. water) giving 166 kg. moist raw material. A slurry with a water content of 40 per cent. contains 100.7 kg. water, so that 250 kg. slurry will be required to produce 100 kg. clinker. The wet process therefore requires 84 kg. more water than the dry process.

The combustion of 1 kg. carbon produces 8,000 kcal., while the heat requirement of the Lellep kiln with an exit temperature of about 100 deg. C. amounts to about 100,000 kcal. per 100 kg. clinker. Fuel consumption with the Lellep kiln has been reduced lately in a few works to less than 90,000 kcal., but for the

present purpose this need not be taken into consideration as variations in the composition of the raw material are apt to cause fluctuations in fuel consumption and the difference may be looked upon as a margin of safety.

As both kilns have the same exit temperature, the excess fuel consumption of the theoretical kiln as compared with the Lellep kiln is entirely due to (1) the heating of the additional water from about 20 deg. C. to 100 deg. C.; (2) evaporation of this water; and (3) heating of the additional exit gases to 100 deg. C.

	kcal.
Item (1) amounts to .. .. . $(100 - 20) \times 84$	= 6,720
According to Mollier the evaporation of water at atmospheric pressure consumes 539.4 kcal. per kg. water, therefore .. .. . $539.4 \times 84$	= 45,310
Total .. .. .	52,030

Item (3) may be calculated as follows. The complete combustion of 1 kg. carbon in the presence of 10 per cent. excess air produces 9.8 cubic metres of combustion gas, which consist of 1.87 cubic metres  $\text{CO}_2$ , 0.19 cubic metres  $\text{O}_2$ , and 7.74 cubic metres  $\text{N}_2$ . The volume of air required is also 9.8 cubic metres.

Taking the mean specific heat of air in the temperature range 0-100 deg. C. as 0.293 and that of carbon dioxide as 0.383, the heat content of the combustion gas is :—

From oxygen and nitrogen content,	kcal.
$(7.74 + 0.19) \times 100 \times 0.293$	= 232
From carbon dioxide content, $1.87 \times 100 \times 0.383$	= 72
Total .. .. .	304
The heat content of the combustion air at 20 deg. C. with a specific heat in the temperature range 0-20 deg. C. of 0.291 .. .. . $9.8 \times 20 \times 0.291$	= 57
Therefore the loss per kg. C. due to the heat of the dry gases .. .. .	= 247

1 kg. C. can therefore provide  $8,000 - 247 = 7,753$  kcal. for the heating and evaporation of the excess water used in the wet process. Thus the additional fuel required for the wet process as compared with the dry process amounts to

$$\frac{52,030}{7,753} = 6.71 \text{ kg. C.}$$

The additional heat consumption is 53,680 kcal. and the total heat requirement for burning cement by the wet process in the ideal kiln is 153,680 kcal.

This result can only serve as an approximate indication of what is to be expected from a kiln of this kind. In particular, according to the design of the kiln the losses by radiation from its external surface may be greater or less than those of the Lellep kiln. The radiation losses depend in the first place upon the size of the kiln. The Lellep kiln is relatively small. If a small efficient apparatus is installed in front of the rotary kiln as a pre-heating stage the magnitude of

the radiation losses will very largely depend upon whether it can be followed by a considerably shorter rotary kiln, or whether it must be used in conjunction with a kiln of normal length.

In calculating the gas temperature at the end of the drying zone the heat losses to the exterior will be neglected as they depend entirely on the type of kiln. It must therefore be borne in mind that the result will certainly be too low. Furthermore, in a kiln it is scarcely possible to locate the end of the drying zone. Hitherto it has been found in all kilns that for a considerable distance both partially calcined and moist material exist together in spite of the fact that calcination does not commence until about 800 deg. C. has been reached. This may be due to part of the carbon dioxide being driven off at a lower temperature or to considerable variations in the temperature of the gases across any section of the kiln. Strong eddies occur in the kiln, and streams of hot gas may occasionally penetrate far into the drying zone before they give up their heat. Finally, and this seems to be the main cause of this phenomenon, even in a kiln with an exit temperature of 100 deg. C. the temperature difference between gas and raw material is particularly great where the gases enter the drying zone. When, therefore, certain portions of the raw material come into unusually intimate contact with the gases they may be heated to decarbonation temperature although other portions of the material in their immediate vicinity may not yet have been completely dried.

None of these phenomena will, however, be taken into account as they make no change in the fundamental conditions, and it will be assumed that there is a point in the kiln at which the material is just free of water and where the material commences to be heated to decarbonation temperature. As water is converted into vapour at 100 deg. C. the material at this hypothetical point must also have a temperature of 100 deg. C. The temperature at which the material enters the kiln will again be taken as 20 deg. C., and it will be assumed that complete combustion has already taken place when the hot gases enter the drying zone. As losses to the exterior are being neglected the total heat content of the hot gases is transferred to the raw material and the water, with the exception of a residue which remains in the dry gases. Thus the perceptible heat of the material and the gas at the moment when the gas enters the drying zone is equal to the amount of heat transferred to the water plus the perceptible heat of the dry material and dry gases leaving the kiln.

The mean specific heat of the dry raw material in the temperature range 0-100 deg. C. is taken as 0.2. For 149.3 kg. of dry material at 20 deg. C. the heat content of the dry material on entering the kiln is  $149.3 \times 20 \times 0.2 = 600$  kcal. The heat content of the material when it leaves the drying zone is

$$149.3 \times 100 \times 0.2 = 2,986 \text{ kcal.}$$

The total heat requirement of the kiln of 153,680 kcal. corresponds to 19.21 kg. C., which produces  $19.21 \times 9.8 = 188.5$  cubic metres of dry gases. This volume comprises  $19.21 \times (7.74 + 0.19) = 152.6$  cubic metres  $N_2O_2$  and 35.9 cubic metres  $CO_2$ . Further, 112 kg.  $CaCO_3$  contain 49.3 kg.  $CO_2 = 25.1$  cubic

metres  $\text{CO}_2$ . The total volume of dry gases entering and leaving the drying zone is therefore the sum of these three items, viz., 213.6 cubic metres.

Assuming a mean specific heat (at 100 deg. C.) of 0.293 for  $\text{N}_2\text{O}_2$  and of 0.383 for  $\text{CO}_2$ , the heat content of the dry exit gases is

$$\begin{array}{r} \text{kcal.} \\ 152.6 \times 100 \times 0.293 = 4,460 \\ 61 \times 100 \times 0.383 = 2,330 \\ \hline \text{Total} \quad 6,790 \end{array}$$

The amount of heat transferred to the water by the kiln gases is  $100.7 \times (539.4 + 80) = 62,374$  kcal. The heat content of the kiln gases on entering the drying zone is therefore  $62,374 + 600 + 6,790 - 2,986 = 66,778$  kcal. From this the temperature of the gases entering the drying zone can be calculated as follows:

$$t = \frac{66,778}{61 (\text{specific heat } \text{CO}_2) + 152.6 (\text{specific heat } \text{N}_2\text{O}_2)}$$

Taking mean specific heat of  $\text{CO}_2 = 0.471$  and mean specific heat of  $\text{N}_2\text{O}_2 = 0.309$ ,  $t = 880$  deg. C. (approx.).

As radiation losses have been neglected it will be necessary to reckon with a gas temperature of 50 to 100 deg. C. higher for most examples of a kiln of this kind. The conclusions which may be drawn with regard to the possibility of using steel as the structural material for the drying zone of the kiln will be discussed later when individual types of kiln are dealt with. The next point to be discussed is the effect of altered working conditions on the temperature at the entrance to the drying zone.

If the kiln is operated with an increased excess of air, but the exit temperature is kept at 100 deg. C., the volume of exit gas and consequently the heat loss will be greater than with the ideal kiln upon which the previous calculation was based. Fuel consumption will therefore be higher. The quantities of heat consumed in the kiln will, however, remain the same. In the drying zone the same heat requirement will obtain but there will be a greater volume of kiln gas to furnish it. As the exit temperature is to remain constant at 100 deg. C., however, the gas must enter the drying zone at a lower temperature than before, and the mean temperature difference between gas and raw material will be smaller. Whether it will be possible in these conditions to transfer the requisite amount of heat to the raw material with the means available in this zone of the kiln must depend entirely upon the design of the apparatus. Presumably an increase in the excess of air would have to be associated with a simultaneous reduction in kiln output unless it were decided to tolerate an increased exit temperature.

If the excess air is kept constant at 10 per cent. and the exit temperature is allowed to rise, which can easily be brought about by increasing the fuel supply, the temperature of the gases entering the drying zone will be raised. As the excess of air is unchanged the flame temperature will be the same as in the

theoretical kiln. The quantity of heat to be transferred to the raw material is likewise the same. In consequence of the higher exit temperature, however, the loss of heat in the exit gas is increased, and with it both the fuel consumption and the volume of gas. In the kiln we then have material with the same heat requirement as before, but a greater volume of gas with the same maximum temperature. The consequence is an increase of gas temperature in all zones except the clinkering zone, as compared with the corresponding temperatures in the theoretical kiln, and thus a higher gas temperature at the entrance to the drying zone.

If excess of air and exit temperature are increased simultaneously, there will be a summation of the effects discussed and some, being counteracted by others, will be cancelled. This applies to the gases entering the drying zone, and conditions here will not be very different from those in the theoretical kiln. But this will be avoided as far as possible on account of the high heat losses which it involves.

An increase in kiln output is always accompanied by a rise in the exit temperature and, as a result, by an increase in heat losses and fuel consumption, due to the manner in which heat is transferred in the rotary kiln. The transfer of heat from the kiln gas to the raw material takes place slowly. In practice it is necessary to have a large surface for the transfer of heat as well as sufficient temperature difference between the two media. As a rule, part of this surface is furnished by the raw material and the remainder by the walls of the kiln and by heat exchange bodies which take heat from the gases and pass it on to the raw material. If the feed of raw material is increased the supply of fuel and the volume of gases must also be increased. The surface available to take heat from the augmented volume of gas is, however, only very slightly larger than before, as there has been no change in the area of the kiln walls and only a relatively insignificant increase of the surface provided by the raw material. The deficiency in heating surface can only be balanced by increasing the temperature difference between gas and raw material. This takes place automatically in every kiln. In each zone the gas temperature rises until the temperature difference is sufficient to ensure that the requisite quantity of heat is transferred to the raw material.

In order to avoid higher heat losses in the exit gas when the output is increased it would be necessary to enlarge the surface available for the transfer of heat. This is impracticable so far as the clinkering and decarbonating zones are concerned; but there are types of pre-heating equipment with which it is possible to adjust the area of the heating surface if necessary during the operation of the kiln. Enlarging the heating surface in the pre-heating zone only leads to an uneven increase in the heat transfer efficiency of the various parts of the kiln and consequently to a shifting of the zones. This is of particular importance when the pre-heating apparatus, which usually encompasses the drying zone, is made of steel. Part of this apparatus, which is not intended to withstand temperatures higher than those of the drying zone, is subjected to



the temperatures obtaining in the decarbonating zone and is burned every time the kiln output is increased, even if no change is made in the size of the heating surface in the pre-heating unit; the only difference is that, if this is not done, the exit temperature is raised and fuel consumption is increased.

When the pre-heating apparatus does not form part of the kiln, packing must be inserted between the kiln and the pre-heating unit to form the connection between the moving and the stationary parts of the installation. It is difficult to keep such joints gastight, and the penetration of air which is apt to occur is the cause of two different effects. In the first place the cold air reduces the temperature of the hot gases entering the pre-heating unit and the risk of the steel parts being burned is diminished. The second effect, which takes place simultaneously, is that the volume of gas is increased and the gas tem-

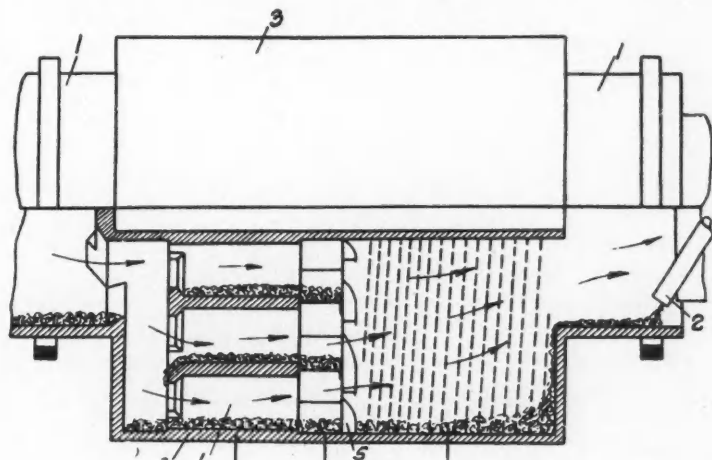


Fig. 1.

perature falls at the entrance and exit of the pre-heating unit. The exit temperature cannot fall below 100 deg. C. as the water content of the raw material must be carried off as vapour. Therefore a greater volume of gas goes into the flue at this temperature than was intended, and this means about the same heat loss as when the whole plant is working with too much excess air.

The pre-heating units that have been described can be classified as follows:

- (1) Units with heat transfer surfaces (a) chains, (b) baffles or cells, (c) heat exchange bodies mixed with the material. (2) Units with layers of raw material.
- (3) Units with slurry sprays.

The apparatus grouped under (2) are only suitable for raw slurry from which part of the water can be removed mechanically so that it can be formed into pellets and spread out as in the Lellep kiln. These units have a high thermal

efficiency, but few slurries can be treated in this manner unless use is made of heat transfer surfaces, especially those of the type (1c). Units of this type will be discussed later in conjunction with those of group 1. Units of the third type suffer from excessive dust formation whenever it is attempted to carry out effective pre-heating with them; for this reason they are falling into disuse.

The units of type 1 function according to one of the following principles: (I) counter current, (II) parallel current, (III) cross current, or (IV) mixing current.

The counter-current system is the simplest, and most readily adapted to the ordinary rotary kiln; for example, it permits the pre-heating unit to be built into the kiln, and the penetration of air with its disadvantages is prevented. The most important characteristic of heat exchange apparatus on this system is that the hottest material is brought into contact with the hottest gases, allowing thorough utilisation of the heat content of the gas because the gases leave the unit at a temperature lower than that at which the material is discharged. Full advantage cannot be taken of this property if pre-heating units do not extend beyond the drying zone. This, however, is the only form possible in practice as the heating surfaces must be of metal in order to be efficient in transferring heat to the relatively cold raw material, and unprotected metal is unable to withstand the temperatures obtaining in the kiln beyond the drying zone. As shown by the calculations given, gases in the hottest part of the drying zone may attain high temperatures, and it will be a cause for satisfaction if the pre-heating unit functions properly over the whole length of the drying zone.

The material leaves the drying zone at about 100 deg. C. and the gases must have at least the same exit temperature. With pre-heating units for slurry it is therefore impossible to make full use of the advantage of the counter-current system.

At the high temperatures of the gases entering the drying zone the steel heating surfaces would burn unless continually cooled by the slurry, which forms a protective layer. This layer is not effective unless it remains intact until fresh slurry is brought into contact with the surface. As drying proceeds the slurry loses its power of adhesion, and it is in the hottest part of the drying zone that the layer of slurry is most deficient. This peculiarity of counter-current pre-heating units has nullified attempts to solve the problem of slurry thickening in this direction; the difficulty has been that the steel heating surfaces in the hottest part of the drying zone have burned away and the remaining surfaces have not sufficed to transfer the requisite heat from the gases to the raw material. It has therefore not been possible to achieve the desired exit temperature of 100 deg. C. in this manner.

An example of the attempts that have been made to overcome this difficulty is illustrated in Fig. 1. The proposal, which has more than one source, is based on the fact that steel heating surfaces are unable to withstand the temperatures in the hottest part of the drying zone, and could be replaced by surfaces of a refractory material. As the durability of these materials is low it would only



be possible to use them as stationary cells, and in order to avoid stoppages the cells should not be too narrow. The extra heating surface provided by the cells is not great and their value is further reduced by the fact that heat is transferred to the raw material less efficiently by a refractory material than by steel. It will be necessary for this reason alone to equip a considerable length of the kiln with cells and this will increase the risk of choking the kiln. In practice only a small number of such cells can be used and only a small part of the desired effect has been achieved.

In kilns of the type shown in Fig. 1 the whole of the drying zone is divided into tubes, the upper parts of which are fitted with chains while the lower parts are provided with cells of ceramic material. This subdivision into tubes makes the cells more accessible, as openings can easily be provided in the ends of the tubes through which incrustation can be removed.

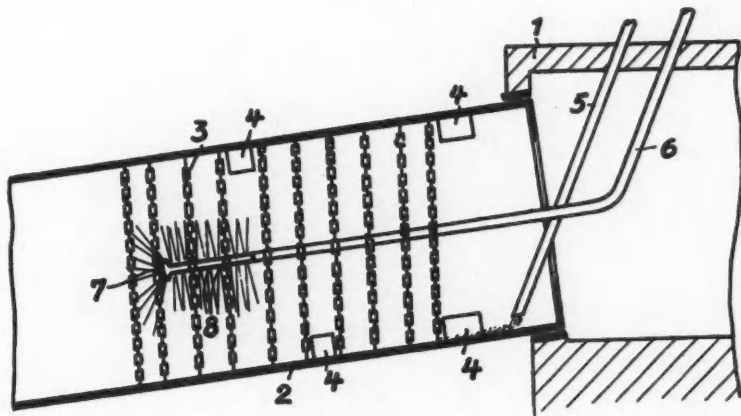


Fig. 2.

The knowledge that ceramic materials do not give good heating surfaces has led to attempts to find another solution to the problem. One of these suggestions is shown in Fig. 2. Slurry is fed, as usual, to the chains in the drying zone through a pipe which terminates just inside the end of the kiln. In addition there is a central pipe which runs into the kiln as far as the section containing the hottest chains, where it terminates in a rose through which a small proportion of the slurry is pumped into the kiln. In this manner the hottest chains, which otherwise would only come into contact with partially dried and therefore poorly adhesive slurry, are continually sprayed with fresh slurry which forms a protective coating. This arrangement makes it possible to extend the zone fitted with chains farther into the kiln, and as the number of heating surfaces is increased the utilisation of the hot gases is improved.

The idea upon which the design is based is good but it is doubtful whether the apparatus will meet with success. The apertures of a rose through which only part of the slurry is to be led would be very small, and as the rose is situated in the interior of the kiln, it would not only be inaccessible but would be exposed to the action of very hot gases. As far as I am aware, the apparatus has not yet been tried out in practice. It would probably be better to dispense with the rose at the end of the central pipe. The hot chains would not be wetted so thoroughly because the fresh slurry would immediately mix with the partially dried slurry and the chains could only gather slurry by dipping into the accumulation at the bottom of the kiln, but it would be worth while to give the apparatus a trial in this form. It is probable that it would succeed in making it possible to use a greater number of chains.

The counter-current system has the advantage of being an excellent dust preventer. Before the dust-laden gases from the interior of the kiln can reach the exit they must pass through the heat exchange units which are covered with wet slurry—and this is a good dust trap.

Parallel-current pre-heating units, in which raw material and gases travel in the same direction, have the advantage that heat transfer takes place rapidly, and this allows the dimensions of the unit to be kept relatively small. Moreover, as the hottest gases come into contact with fresh material which wets the heat-exchange surfaces there is no fear of burning. So far there would seem to be no objection to including the whole of the drying zone in the pre-heating unit, but this is impossible for a different reason; if this were done the exit gases would come into contact with completely, or almost completely, dry material and would carry off large quantities of dust. For this reason the treatment in the pre-heating unit must be restricted to a partial drying of the material. In this respect the possibilities of the parallel-current unit seem to be similar to those of the mixing current units discussed later. No parallel-current pre-heating units appear to have been built yet, and it is doubtful whether the idea will be pursued as this apparatus has the same advantages and disadvantages as the mixing-current units which, however, on account of their design are more readily adapted for use with the rotary kiln.

The cross-current system, in which the paths of the two media cross each other, is used in heat exchange appliances of the most diverse types, e.g. in water-tube boilers and in air pre-heaters. In the cement industry it was probably used for the first time in the design of pre-heating units for rotary kilns by Lelupp, who employs it for the dry process in the form of a moving grate upon which the material is spread and through which the gases are passed downwards in a direction at right angles to the path of the material. It has been indicated that it is only possible to use apparatus of this kind with slurry if the material can be thickened sufficiently beforehand by other means. This objection does not apply, however, if use can be made of heat exchange surfaces, preferably in the form of heat exchange bodies mixed with the raw material. There are two ways of doing this: (1) either steel heat exchange bodies in the form of short

lengths of tube or steel section can be used, in which case the heat exchange bodies must be separated from the raw material after it has passed through the pre-heating unit and mixed with fresh slurry for the repetition of the process; or (2) the heat exchange bodies may be composed of a refractory material, e.g. finished clinker, and allowed to pass with the raw material through the pre-heating unit and the kiln. Part of the clinker leaving the cooler is then mixed with fresh slurry and taken back to the pre-heating unit.

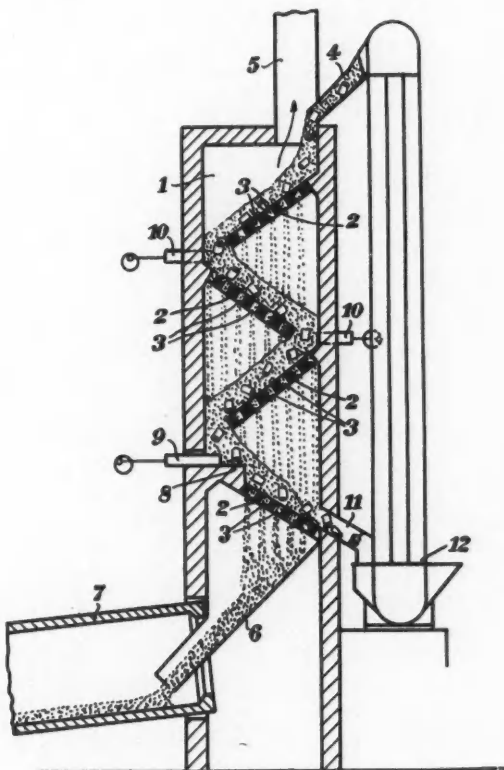


Fig. 3.

A unit in which the heat exchange bodies pass through the pre-heater only is illustrated in Fig. 3. The mixture of raw material and heat exchange bodies passes downwards over a series of sloping screens arranged in zig-zag fashion. The exit gases from the rotary kiln flow upwards through the screens and the material passing over them. The slope of the screens is so arranged that the mixture of slurry and heat exchange bodies rolls or slides downwards under

its own weight. When the mixture arrives on the lowest screen the raw material should have been dried to such an extent that most of it separates from the heat exchange bodies and falls through the openings in the screen on to the chute beneath and thence into the kiln. No harm is done if particles of raw material come away from the heat exchange bodies before reaching the lowest screen, as they can only fall on to the next screen below and cannot drop on to the chute until they are so dry as to be unable to adhere to the heat exchange bodies. In this way only properly dried material can pass into the kiln. The size of the heat exchange bodies is such that they cannot pass through the openings in the screens. After the heat exchange bodies have given up all the raw material—or the greater part of it—on the lowest screen they fall into the bucket of a conveyor where they are immediately covered with fresh slurry and then brought back to the uppermost screen.

New material flows down the screens in proportion to the rate at which the heat exchange bodies are removed at the bottom, so that all the screens are continually covered with a layer of raw material and heat exchange bodies. The depth of the layer is regulated by the distance between the lower edge of one screen and the top of the next below. The adhesion of individual bodies can be prevented by the use of fairly large heat exchange bodies so that the depth of the layer is about equal to the diameter of one of the bodies. This will also reduce to a minimum the resistance to the passage of the gases through the layers of raw material. The supply of material to the lowest sieve is regulated by a horizontal step at its upper edge and a sliding gate. Slides can also be provided to prevent stoppages between the screens. If the dry material tends to adhere to the heat exchange bodies a rotary screen may be fitted between the lowest screen and the conveyor.

It is not to be anticipated that the heat exchange bodies will be burned by the hot exit gas; their temperature cannot rise above that of the raw material, and this will not be above 100 deg. C. as the whole unit works within the drying zone. It is only possible for the temperature of the metal to rise occasionally above the permissible limit in those places where the raw material has already parted from the heat exchange bodies and these are exposed without protection to the action of the hot gases. This is most likely to happen on the bottom screen, but the flow of material can be regulated by the gate so that the bodies are not exposed to the gases long enough for burning to take place.

As the movement of the raw material and the heat exchange bodies in the unit is very small there will not be much dust, and ample opportunity is provided for such dust to settle on the layers of wet material. If the screen apertures should choke, the perforated screens could be replaced by sloping grates and the individual bars could be cleaned by shaking. This procedure could not be applied in the case of the lowest screen which is exposed to the fresh hot gases and must therefore be built of refractory material. It would, however, be possible to overcome this difficulty by reconstructing the unit so that the gases pass downward through the lowest screen, which would then be protected by the

layer of raw material. On the whole, there seems no reason why the unit should not succeed in completely drying the raw material. The reason why it has not yet been tested on a sufficiently large scale is to be found in the present economic depression.

The operation of a system in which the heat exchange bodies pass through the whole length of the kiln will be demonstrated by reference to a Lellep kiln (see Fig. 4). Behind the cooler, which is beneath the kiln, there is an apparatus which sorts the clinker according to size, the coarse material being transported to the clinker store and the finer material being fed to a conveyor worm where it is mixed with fresh slurry. This mixture must contain so much clinker that it has a granular structure and can be spread upon the moving grate, after which the material is treated as in the dry process. Any material that may fall through

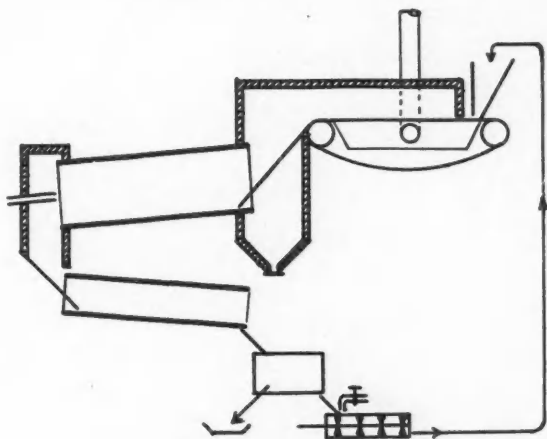


Fig. 4.

the grate is returned to it with the raw material. The system has the advantage that there can be no possibility of the heat exchange bodies being burned as these consist of clinker. Thus it is possible to extend the scope of the pre-heating unit well into the decarbonation zone, i.e. we have a relatively small kiln and the same thorough removal of dust from the exit gas as with the Lellep kiln.

Closer examination of the system reveals serious faults. If the slurry is to be given a granular structure its water content must be reduced to about 20 per cent. To every 2.5 kg. of slurry with 40 per cent. of water (which corresponds to 1 kg. clinker) an equal quantity of clinker must be added to reduce the water content to 20 per cent. This means that the quantity of clinker passing through the clinkering zone and the cooler will be  $3\frac{1}{2}$  times the output of the kiln. If this large quantity of clinker passes into the cooler the available air will not be enough to cool the clinker sufficiently. The heat content of that portion of the clinker which is mixed with the raw slurry will not be lost, for it serves to

warm the slurry and to evaporate some of the water, but the heat in the finished clinker which is removed to the clinker store cannot be recovered and is a total loss. The following approximate figures will have to be taken into consideration : three times the quantity of clinker produced passes through the kiln and the clinker then leaves the cooler at about 500 deg. C. Out of every 3 kg. of clinker, 1 kg. is taken to the clinker store and 2 kg. are mixed with fresh slurry. The heat content of the clinker is sufficient to heat the slurry to 100 deg. C. and to evaporate 18 per cent. of its water content. The remaining water represents about 20 per cent. of the mixture. At the same time the air in the cooler is pre-heated to about 900 deg. C.

The procedure can be altered by separating the circulating clinker from the finished clinker before the latter enters the cooler, and only the normal quantity of clinker passes through the cooler that can be sufficiently cooled. In order to

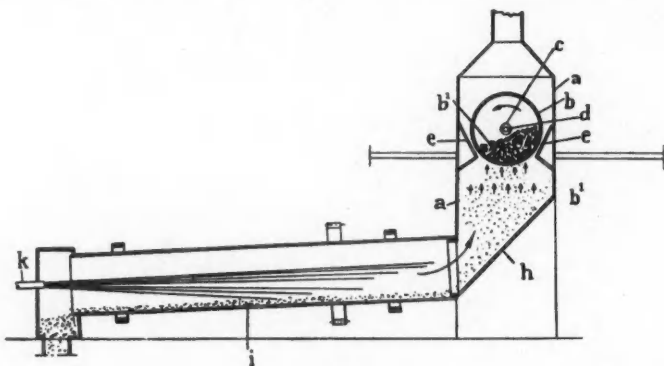


Fig. 5.

exploit the heat content of the circulating clinker to the best advantage this portion of the clinker must be mixed with the raw slurry as soon as it emerges from the kiln. This could be done in a granulating unit, such as is used for blast-furnace slag. By adopting this procedure it would be possible to work with a quantity of circulating clinker about equal to that of finished clinker. There would, however, be no objection to having a greater quantity in circulation if necessary. If it is considered that the mixture of raw slurry and clinker may only contain small fragments of clinker in order to avoid stoppages and to bring an approximately homogeneous material on to the moving grate, it will be obvious that this procedure must be fraught with serious difficulties, apart from the fact that it is doubtful whether it will be possible to avoid considerable heat losses in the granulator.

The most developed and tested of modern pre-heating units is one that operates on the mixing-current system and is shown in Fig. 5. It consists of a perforated drum, about half full of heat exchange bodies, which rotates about a horizontal axis in front of the rotary kiln. The raw slurry runs on to this



drum, which it enters through perforations in its wall. Inside the drum the slurry is intimately mixed with heat exchange bodies consisting of lengths of steel tube or bar. The exit gases from the kiln flow upwards through the drum at right angles to its axis. The drum is provided with a casing which fits close to its sides so as to ensure that the gases flow through the drum and not around it. Gastight packing is not required, as the heat exchange bodies are fairly large (10 cm.) and the gas-permeability of the drum and its content is therefore high. The portion of the charge at the bottom of the drum will be the first to come into contact with the hot gases, but owing to the rotation of the drum it will be immediately carried up and a few moments later will fall back again; during this time it will have come into contact with fresh slurry and will have been effectively cooled. The cumulative effect is that the whole contents of the drum will attain the same temperature, i.e. 100 deg. C. (the boiling point of water), due to the fact that the contents of the drum are continuously mixed, hence the designation "mixing-current system." The greatest temperature differences are probably in the wall of the drum which is exposed alternately to the hot gases and the cold slurry.

In this process, as in the parallel-current process, heat transfer takes place very rapidly and the unit is characterised by its compact design. As regards dust it is not so favourable; the dried portions of the material are continually thrown up into the path of the exit gas and it is almost inevitable that a certain amount of dust should be carried off. This is not prevented by the continuous rain of fresh slurry upon the heat exchange bodies, as drying is almost instantaneous. Experience has shown that the material emerging from the drum is uniformly dried no matter to what degree the unit has been adjusted. Such uniformity could not be achieved if the drying process continued for any considerable period of time; if this were the case the vigorous movement of the contents of the drum would result in the occasional separation of dry and moist material from the heat exchange bodies. As this does not happen it may be taken that drying takes place very rapidly, in fact, it must be completed in the short space of time required for a heat exchange body to travel from the top of the heap of bodies where it comes into contact with the fresh slurry to the floor of the drum. This is frequently only a second, or even less.

Associated with this vigorous movement of the heat exchange bodies is a further advantage peculiar to units of this type, namely, the ease with which the dried material is separated from the heat exchange bodies and the absence of any trouble from adhering crusts. Obviously the more complete the drying in the drum the more easily will the material come away from the heat exchange bodies; if for any reason the material is to be only partially dried in the drum, incrustation can be prevented by increasing the speed at which the drum revolves.

The only defect from which the unit suffers is the formation of dust. It has been found in practice that the loss of dust can be almost entirely avoided by refraining from completely drying the material in the drum. The degree of dryness which can be achieved without excessive dust production depends upon the nature of the raw materials. Generally, however, the water content of the

material can be reduced to about 12 to 15 per cent. Adjustment to any given degree of dryness can be carried out by varying the quantity of heat exchange bodies. The unit is therefore efficient, readily adjustable, and able to satisfy all the requirements.

The following must be borne in mind if it is desired to add the unit to a rotary kiln plant so that an exit temperature of 100 deg. C. is achieved. The first condition is that the plant as a whole shall comprise a sufficiency of heating surface. If this is not available the desired exit temperature cannot be achieved. The pre-heating unit must contain a definite amount of heating surface which will depend upon the degree of dryness the raw material may attain and still give more or less dust-free exit gases. The remainder of the requisite heating surface must therefore be in the kiln. If the unit is followed by a plain rotary kiln, the kiln must be long enough to furnish all the heating surface required. The length of the kiln is governed by the output desired and the temperature at which the gases must pass from the kiln into the drum. The temperature can be deduced from the fact that the drying zone will extend a little beyond the pre-heating unit into the rotary kiln. Presumably it will be necessary to make the kiln as long as an ordinary rotary kiln working with an exit temperature of about 400 deg. C. As a matter of fact, the gases will enter the drum at a considerably higher temperature, but it must be remembered that in the ordinary wet-process kiln a cold wet slurry is fed into the upper end of the kiln, which absorbs heat avidly from the gases, while in the present case the slurry that enters the kiln has already been dried to a very considerable extent. The working conditions are in this case much more like those of the dry process, and a kiln of a length which would suit dry-process conditions will probably be most satisfactory.

If these considerations are borne in mind a wet-process plant can be installed which will operate with an exit temperature of 100 deg. C., but only for a certain given output. If the output is to be increased it will be necessary to make a corresponding increase in the amount of heating surface. This can only be done in the pre-heating unit, and the result is that the material in the unit will be more completely dried and the formation of dust will commence. If the number of heat exchange bodies in the pre-heating unit is reduced until the dust formation ceases the amount of heating surface available in the plant will be inadequate and the exit temperature will rise above 100 deg. C. Much the same applies if the rotary kiln is too short. With the designed output the kiln will not provide sufficient heating surface to transfer so much heat to the raw material that the gases are cooled to the temperature corresponding to the entrance to the drying zone in the theoretical kiln, and the exit temperature will then be higher than 100 deg. C. If an attempt is made to increase the number of heat exchange bodies in the pre-heating unit, drying will proceed too far and the formation of dust will begin.

Although it is possible to achieve an exit temperature of 100 deg. C. by a slurry-drying drum working on the mixing-current system, this can only be done if a certain kiln output is not exceeded.

## The Hardening and Corrosion of Cement.—VIII.

By Dr. KARL E. DORSCH.

(OF THE TECHNICAL HIGH SCHOOL, KARLSRUHE, BADEN.)

### Effect on Corrosion of Temperature of Salt Solutions.

THE corrosion experiments showed that the rate at which test-pieces were attacked varied in summer and winter, being more rapid in summer when the mean temperature is higher. This obviously depends on differences of temperature of the solutions containing the test-pieces, the temperature of which, with that of the storage chamber, varies with the seasons. It was, therefore, decided to undertake an accurate investigation into the effect of temperature on the decomposition of mortar and concrete, keeping all other conditions constant. Cement cubes measuring 3 cm. were used for this work. The percentage analysis of the high-strength Portland cement used was insoluble residue, 0.45; loss on ignition, 2.17;  $\text{SiO}_2$ , 20.90;  $\text{CaO}$ , 65.44;  $\text{Al}_2\text{O}_3$ , 6.38;  $\text{Fe}_2\text{O}_3$ , 3.12;  $\text{MgO}$ , 1.46;  $\text{SO}_3$ , 1.75. The residue on the 76 sieve was 0.20 per cent. and on the 180 sieve 7.3 per cent. A proportion of 27 per cent. of mixing water was used, and the temperatures of the water, gauging room, and storage chamber were maintained constant at 18 deg. C. Only the temperatures of the salt solutions were varied. The solutions used were 15 per cent. sodium and ammonium sulphate. The humidity of the gauging room was 50 per cent.

The cement cubes were stored 1 day in air and 6 days in water before being immersed in the salt solutions. These solutions were maintained at three different mean temperatures, one series at  $-5$  deg. C., the second at  $+15$  deg. C., and the third at  $+30$  deg. C. At 30 deg. C. the water which evaporated was replaced daily. The attack in ammonium sulphate at the various temperatures proceeded as follows.

AT  $-5$  DEG. C.—At the end of 2 days the test-piece was unattacked. After 3 days one of the upper edges showed slight attack at one point, and after 5 days three edges were similarly affected. In 7 days the attack had slowly spread from these points and the cement had to some extent broken away. Up to 11 days decomposition only proceeded very slowly and there was no distinguishable difference compared with the cube after 7 days. The cube at 11 days is shown in Fig. 64 (left). At 23 days (Fig. 65, left) there was no obvious difference from the results after 11 days, i.e., the attack did not appear to have progressed farther.

AT  $+15$  DEG. C.—There was no sign of attack after 1 day, but after 2 days certain of the edges were slightly attacked. In 3 days the attack had spread around the original points and in 5 days all the edges had begun to break away. After 7 days decomposition was only slowly proceeding and the edges were covered with a white crystalline powder. Attack was still slow after 11 days (Fig. 64, centre) and the appearance of the cube was very little different from that at 7 days. Up to the end of 23 days attack had still proceeded slowly (Fig. 65, centre), but nevertheless, much more rapidly than at  $-5$  deg.

AT + 30 DEG. C.—There was no attack after 1 day, but at  $1\frac{1}{2}$  days the edges had lost strength. In 2 days the edges were visibly attacked at certain points, and after 3 days both edges and corners were seriously affected and tended to break off. After 5 days the edges had completely broken away and the entire surface of the cube was affected, while in 7 days the surface was completely destroyed. The decomposition had proceeded much farther after 11 days (Fig. 64, right). In 23 days the test-piece was badly decomposed and the bottom of the container was covered with fragments. After 30 days the cube was completely disintegrated to a muddy mass.

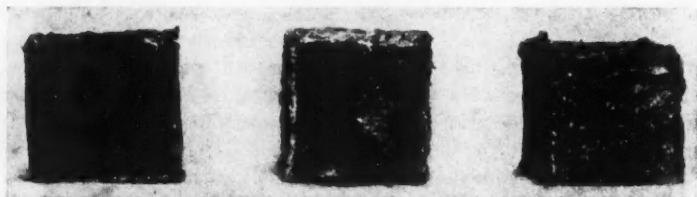


Fig. 64.—Cement cubes after 11 days' storage in ammonium sulphate solution at - 5 deg. C. (left), + 15 deg. C. (centre), and + 30 deg. C. (right).

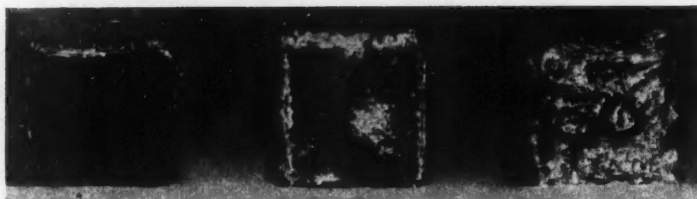


Fig. 65.—Cement cubes after 23 days' storage in ammonium sulphate at - 5 deg. C. (left), + 15 deg. C. (centre), and + 30 deg. C. (right).

The results obtained by storage in sodium sulphate solution are identical with those shown in Figs. 64 and 65, with the sole difference that longer times are required to attain them. The temperatures chosen for these experiments approximate to the summer and winter temperatures and the results thus relate directly to practical conditions.

It has already been pointed out that the decomposition of cement by sulphates or other aggressive salt solutions depends on reaction between the  $\text{Ca}(\text{OH})_2$  set free by the cement and the ions of the solution, with the formation of calcium salts which are dissolved out of the mortar. The effect of temperature on the velocity of such ionic reactions is considerable. Not only are the ionic velocities of the reaction components increased, so that the  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{SO}_4$  or  $(\text{NH}_4)_2\text{SO}_4$  more rapidly interact, but also the solubilities of the reaction products are increased by raising the temperature. The following summary shows the

extent to which the solubility of  $\text{CaSO}_4$  in water varies with temperature, the figures giving the number of grammes of  $\text{CaSO}_4$  dissolving in 1,000 c.c. of water.

0 deg. C.,	1.946 g.	50 deg. C.,	2.180 g.
18    ,,	2.110 g.	70     ,,	2.082 g.
24    ,,	2.164 g.	100   ,,	1.810 g.
38    ,,	2.218 g.		

$\text{CaSO}_4$  dissolves extremely readily in  $(\text{NH}_4)_2\text{SO}_4$  solution with the formation of the double salt  $\text{CaSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , the production of which affords a further explanation of the relatively powerful chemical action of  $(\text{NH}_4)_2\text{SO}_4$  solutions on cement and concrete. The solubility of this double salt is more strongly affected by increase of temperature than that of  $\text{CaSO}_4$ .

The solubility of  $\text{CaSO}_4$  is further greatly increased by the presence of  $\text{NaCl}$ ,  $\text{KCl}$  and  $\text{NH}_4\text{Cl}$ , and this effect increases rapidly with temperature. This is of great importance in marine construction. Sea-water contains 3 to 3.5 per cent. of salts, which consist approximately of 78 per cent.  $\text{NaCl}$ , 2 per cent.  $\text{KCl}$ , 9 per cent.  $\text{MgCl}_2$ , 6.5 per cent.  $\text{MgSO}_4$  and 4 per cent.  $\text{CaSO}_4$ . The chlorides in sea-water considerably increase the solubility of the  $\text{CaSO}_4$  formed by the attack of the water on concrete.

These experiments prove the great importance of temperature in influencing the attack of salt solutions on concrete. This effect must be taken into consideration in all experimental work: absolute constancy of temperature and a record of the precise temperature of experiment are essential in all such work. Obviously, also, the effect of temperature is no less important under practical conditions than in the laboratory. The extent of attack of sea-water on concrete will vary with climate: in warm climates more rapid attack must be expected than in cold. It follows that more resistant cements must be used in hot climates and that much greater precautions must be taken to avoid failures arising from the corrosion of the concrete.

#### Effect of Surface Area and Quantity of Test-pieces on Attack by Salt Solutions.

The surface area and quantity of the test-pieces will have a definite effect on the rate of decomposition, in the same way as will the concentration of the attacking solution. It is obvious that with equal quantities of solution of the same concentration varying degrees and rates of decomposition are to be expected when the exposed surface area and number of immersed test-pieces are different. Consider for example two vessels, each containing 4,000 c.c. of solution, but one with 2 and the other with 20 test-pieces immersed. The same amount of salt is available to decompose the mortar in the two cases; it must be concluded that with 20 test-pieces the solution will be consumed before it is able to penetrate deeply into the mortar, while with 2 test-pieces the mortar will be seriously decomposed with hardly any weakening of the solution. In other words, the final concentration of the solution will depend upon the exposed surface area and the number of the test-pieces. The correctness of this point of view, which is of the greatest importance in evaluating the results of investigations, was proved experimentally as follows.

High-strength Portland cement of the following percentage composition was used: loss on ignition, 1.44; insoluble residue, 0.85;  $\text{SiO}_2$ , 19.61;  $\text{CaO}$ , 65.08;  $\text{Al}_2\text{O}_3$ , 5.18;  $\text{Fe}_2\text{O}_3$ , 2.74;  $\text{MgO}$ , 1.80;  $\text{SO}_3$ , 2.59; difference, 0.71. Standard mortar test-pieces were prepared using 8 per cent. water, and these were stored in 4,000 c.c. of 15 per cent.  $(\text{NH}_4)_2\text{SO}_4$  solution. The temperatures of gauging room, storage room, and salt solution were all 18 deg. C. Two experiments were carried out, 3 test-pieces being stored in one container and 24 in the second. The test-pieces were stored 1 day in air and 6 days in water before immersion in the salt solution. Observations were then made daily with the following results.

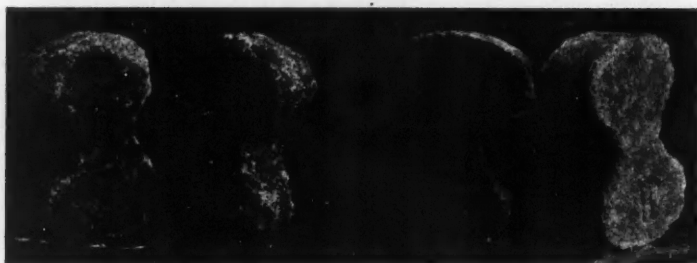


Fig. 66.—High-strength Portland cement after 30 days in ammonium sulphate solution: Left, 3 test-pieces in 4,000 c.c. solution; right, 24 test-pieces in 4,000 c.c. solution.



Fig. 67.—High-strength Portland cement after 80 days in ammonium sulphate: Left, 3 test-pieces in 4,000 c.c. solution; right, 24 test-pieces in 4,000 c.c. solution.

Three test-pieces in 4,000 c.c. solution.—After 4 days the surface of the test-pieces was spongy and soft. Cracks appeared in 8 days, and after 17 days the edges were severely attacked. Fig. 66 (left) shows the test-pieces after 30 days, and Fig. 67 (left) after 80 days when they were completely decomposed.

Twenty-four test-pieces in 4,000 c.c. solution.—The first signs of attack appeared after 24 days when the edges began to break away. This was accentuated after 30 days (Fig. 66, right), but decomposition then proceeded slowly and at 80 days (Fig. 67, right) the test-pieces had practically the same



appearance as at 30 days. Even after 200 days the test-pieces were not completely decomposed.

It appeared important to prove that these results were due to the salt solutions being consumed at different rates, i.e., to differences in the concentrations of the solutions. With this object the solutions from the two containers were analysed every 2 days. It was found that while the solution containing 3 test-pieces scarcely changed during 80 days (the concentration dropped from 15 to 14 per cent.), with 24 test-pieces the concentration sank in a few days from 15 to 12 per cent. and after 30 days only amounted to 8 per cent. In the latter case the attacking power of the salt solution was reduced almost to one-half of the original value in 30 days, while with 3 test-pieces in storage the original concentration of 15 per cent. exerted its effect almost unchanged. The experiments show that the quantity and surface area of the immersed test-pieces and the amount of salt solution have an important effect on the results, which must be taken into consideration in comparative experiments. They also show that the rate of attack depends on the concentration of the solution.

#### **Effect of Preliminary Storage on the Resistance of Cement to Chemical Attack.**

Anderegg<sup>31</sup>, in recent work on the effect of sulphates on the setting and hardening of Portland cement, has shown that an addition of sulphate to setting cement must increase its resistance to sulphate solutions. Calcium sulphate and sulpho-aluminate are formed under these conditions, with increase of volume, while the cement is still elastic and capable of expansion; if these compounds are formed in cement which has already hardened they lead to expansive splitting of the test-pieces. These results lead us to expect that a cement which is stored in sulphate solution shortly after gauging will be more resistant than a cement which is stored for a longer period in air before immersion in the solution. These considerations led the author to an investigation of the manner in which the resistance of cement to salt solutions depends upon the initial conditions of storage.

Ordinary Portland cement of the following percentage composition was used: loss on ignition, 1.96; insoluble residue, 0.82;  $\text{SiO}_2$ , 21.22;  $\text{CaO}$ , 63.55;  $\text{Al}_2\text{O}_3$ , 6.57;  $\text{Fe}_2\text{O}_3$ , 2.59;  $\text{MgO}$ , 1.60;  $\text{SO}_3$ , 1.72. Standard tensile test-pieces were prepared with 8.37 per cent. water. The temperatures of gauging room, storage chamber and salt solutions were all 18 deg. C. The salt solutions used were 15 per cent.  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$ , and in every case 10 test-pieces were stored in 4,000 c.c. of solution. Before immersion in the solutions the test-pieces were submitted to various different sequences of preliminary storage, as follows: (1) 1 day in moist air, 1 day in water; (2) 1 day in moist air, 6 days in water; (3) 1 day in moist air, 13 days in water; (4) 1 day in moist air, 6 days in water 7 days in air (combined storage); (5) 1 day in moist air, 27 days in water; (6) 1 day in moist air, 6 days in water, 21 days in air (combined storage). The times which elapsed before decomposition began under preliminary storage conditions (1) to (6) are summarised below.

<sup>31</sup> Anderegg. Unpublished work (1929).

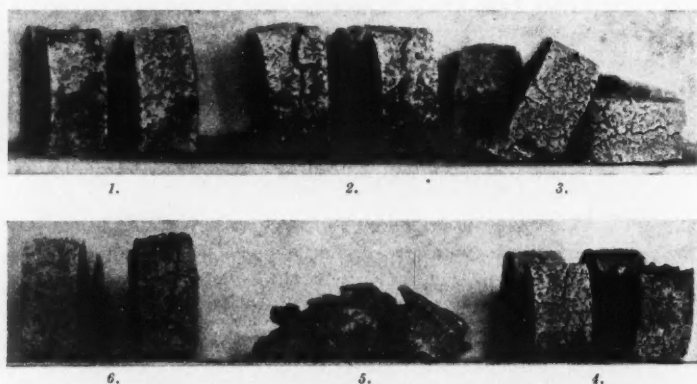


Fig. 68.—Ordinary Portland cement after 7 months in  $\text{Na}_2\text{SO}_4$ . (1) 2 days, (2) 7 days, (3) 14 days' preliminary water storage, (4) 14 days' combined, (5) 28 days' water, (6) 28 days' combined preliminary storage.

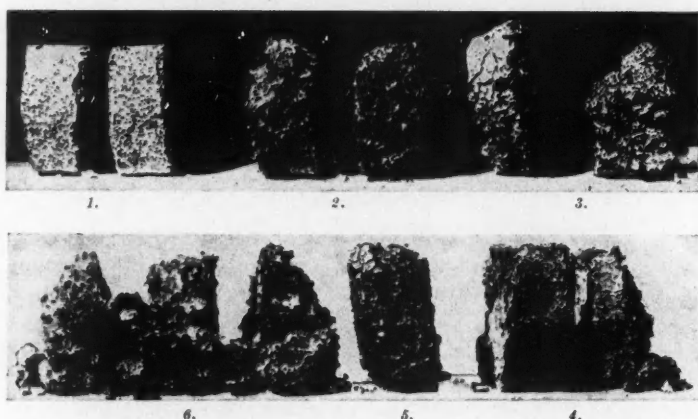


Fig. 69.—Ordinary Portland cement after 1 year in  $\text{Na}_2\text{SO}_4$ . (1) 2 days, (2) 7 days, (3) 14 days' preliminary water storage, (4) 14 days' combined, (5) 28 days' water, (6) 28 days' combined preliminary storage.

NUMBER OF DAYS BEFORE ATTACK IN  $\text{Na}_2\text{SO}_4$  AND  $\text{MgSO}_4$  SOLUTIONS, FOR PRELIMINARY STORAGE CONDITIONS (1) TO (6).

Preliminary Storage.	1	2	3	4	5	6
$\text{Na}_2\text{SO}_4$	144	78	83	83	83	III
$\text{MgSO}_4$	260	40	187	187	164	220

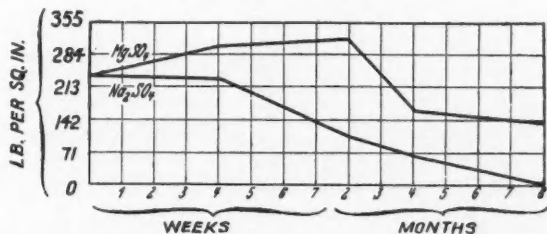


Fig. 70.—Tensile strength: 2 days' preliminary storage.

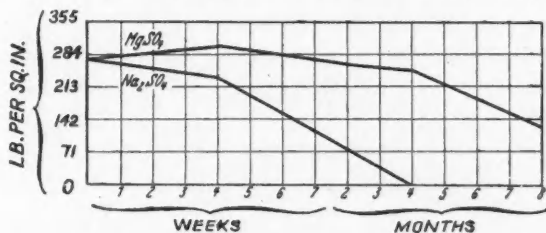


Fig. 71.—Tensile strength: 3 days' preliminary storage.

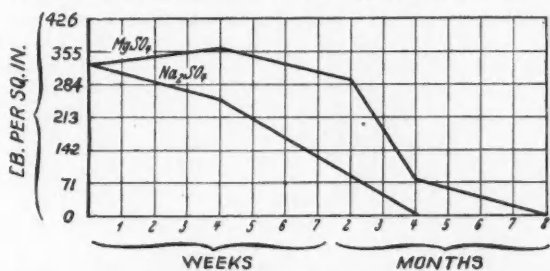


Fig. 72.—Tensile strength: 7 days' preliminary storage.

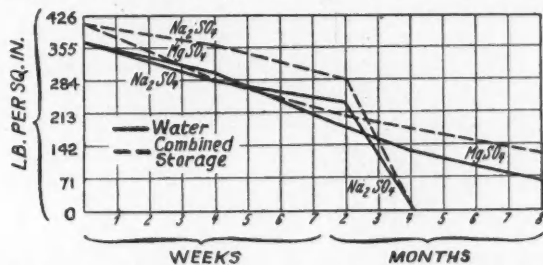


Fig. 73.—Tensile strength: 14 days' preliminary storage.

It is seen from this summary that the longest time elapsed before any sign of decomposition became evident in the case of the test-pieces which were immersed in the salt solutions after the short period of 2 days. Particularly striking is the

low resistance of the test-pieces subjected to 28 days' water storage before immersion in the salt solutions (see Figs. 68 and 70, test-pieces 5).

Figs. 70-75 show the results of tensile tests made at periods up to eight months for the various types of preliminary storage. In the first place, the curves show the more severe attack of  $\text{Na}_2\text{SO}_4$  as compared with  $\text{MgSO}_4$ . They further show that the strength of the test-pieces immersed in aggressive solutions after a preliminary storage of 2, 3 and 7 days may at first rise, but with 14 and 28 days' preliminary storage the strength at once falls considerably. Finally, it is proved

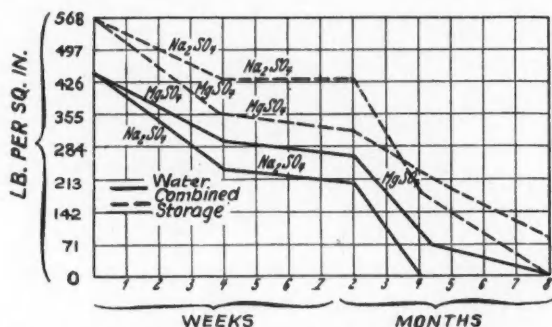


Fig. 74.—Tensile strength: 28 days' preliminary storage.

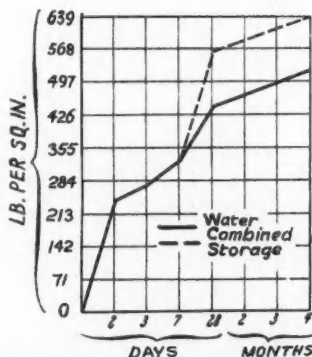


Fig. 75.—Comparative strengths of Portland cement after 2, 3, 7 and 28 days' preliminary storage.

that the resistance of a cement to aggressive solutions is strongly affected by the nature and duration of the preliminary storage. The tests employing 14 and 28 days' preliminary storage clearly indicate that initial water storage has an especially adverse effect. This may be explained by the saturation of the cement with water, which enables the attacking solution to penetrate easily into the interior of the test-piece. The high resistance of the cement subjected to 2 days'

preliminary storage is explained by the fact that the salts formed by the interaction of cement and solution, i.e., those which lead to later decomposition, are in this case produced while the cement is still elastic, of low strength, and unimpaired by expansion.

Other factors which influence the resistance of cement and mortar to the attack of salt solutions are the water-cement ratio, the mixing temperature, the fineness of the cement, and the humidity of the air. Researches on these factors will form the subject of a later publication. Investigations into chemical means of increasing the resistance of cements to attack, with which partial practical success has already been attained, will also be communicated later. Only when the principles elaborated in these articles are generally appreciated and applied will researches on this subject lead to definite progress.

(Concluded.)

---

---

## Effect of Ashes and Stone on the Properties of Portland Cement.

PROF. DR. R. GRÜN and Dr. Hugo Beckmann describe tests made with cements containing ashes from pulverised-fuel furnaces and with cements containing ground stone (*T.I.Z.*, 70/71/1933). Reference is made to the admixture of puzzolana in Italy and trass in Germany. While the authors agree that there is certain justification for using such materials as are in themselves hydraulic, the admixture of sand, ashes and stone is condemned. Tests were carried out with cements containing ash from pulverised-coal furnaces and with cements diluted with ground slate. The results obtained are stated as follows:

Cements diluted with ground minerals of no (or little) hydraulic value are inferior to undiluted cements or cements which contain additions of highly hydraulic material. The cause of this inferiority is the fact that such minerals dilute the cement, so that concrete prepared from such mixtures contains a lower proportion of Portland cement than is indicated in the mix. Lowering of the lime content—claimed to be an advantage—is obtained by the addition of minerals that are practically free from lime or very rich in silica. A low lime content in this case does not provide the characteristics usually associated with a Portland cement of low lime content. In the latter case the cement contains 100 per cent. hydraulic materials. Additions to cement must therefore consist of hydraulically active materials and not of insoluble materials of no hydraulic value. Additions of sand—although in itself resisting the influence of acids—do not improve the durability of the cement in the presence of acids. Such additions act exactly like sand used in the preparation of concrete.

Density, proportion of cement, age, and the characteristics of the cement are the deciding factors in the durability of concrete when exposed to acids. Such (insoluble) parts of the cement as do not actively join in the setting and hardening are diluents only, and are therefore undesirable even if they produce a cement with a low overall lime content.

## The Chemical Constitution of Portland Cement Clinker.

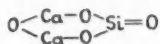
By W. WATSON, B.Sc., and Q. L. CRADDOCK, M.Sc.

(Continued.)

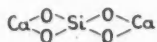
### Early Theories of Solid Solution.

MICHAELIS.—The views of Michaelis,<sup>23</sup> which had mainly a theoretical basis, differed from those of Le Chatelier and Törnebohm. He believed that tricalcium silicate did not exist in Portland cement clinker but that Alite consisted of solid solutions of calcium oxide in less basic silicates and aluminates. Belite he regarded as  $3\text{CaO} \cdot 2\text{Al}_2\text{O}_3$  which had escaped solution by the silicates; he thought this was so because its characteristics seemed similar to those of the "synthetic compound  $3\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ ." Celite he considered to consist essentially of dibasic lime compounds, especially dicalcium ferrite,  $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ , dissolved in dicalcium silicate. Felite he thought was an inactive form of dicalcium silicate whose formation could be prevented by quenching the hot clinker rapidly.

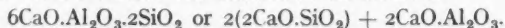
Zulkowsky<sup>24</sup> failed to prepare tricalcium silicate and considered its existence improbable and not proved. He considered that the principal hydraulic constituent of Portland cement clinker is dicalcium metasilicate



which on slow cooling changed into the orthosilicate



This change is accompanied by an increase in volume and decrease of specific gravity of 9.7 per cent., and thus considerable decrepitation occurs. He prepared what he called a normal cement by burning a mixture in the proportion of six molecules of calcium carbonate to one molecule of Zettlitzer kaolin, a material corresponding almost exactly to the formula of kaolinite. He said the product was a high grade white cement and must have the formula



If ferric oxide were substituted for alumina he thought a similar result would be obtained, viz.,  $2(2\text{CaO} \cdot \text{SiO}_2) + 2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ . He maintained that the main constituents of Portland cement clinker are  $2\text{CaO} \cdot \text{SiO}_2$  and  $2\text{CaO} \cdot \text{R}_2\text{O}_3$  and that the presence of tricalcium silicate is not necessary for the production of a good Portland cement. Any calcium oxide above that necessary to form  $2\text{CaO} \cdot \text{SiO}_2$  and  $2\text{CaO} \cdot \text{R}_2\text{O}_3$  forms a solid solution.

HENDRICKX<sup>25</sup> distinguished between fusion and clinkering. In fusion he considered that complete combination occurs and that the value of the product depends only on the elementary composition. The theories and formulæ of earlier investigators are applicable in this case only. In clinkering, however, the



experiences which one attains with one cement raw meal of a given composition may not necessarily apply to another material of the same composition. Where fusion or complete combination does not occur, therefore, the value of the product depends on three main factors: (1) the chemical composition; (2) the physico-chemical state of the constituents; and (3) the temperature and period of burning. He emphasised that the soundness of the product will depend largely on the efficiency of the burning. He considered that ordinary burning practice can never produce all the silica in the form of tricalcium silicate but that solid solutions of calcium silicates in one another or solid solutions of calcium oxide in calcium silicates are produced. The solid solution is the principal constituent of commercial Portland cement clinker and has the probable formula  $2.5\text{CaO} \cdot \text{SiO}_2$ . The alumina and iron oxide he believed to be present as the tribasic calcium salts, and his general formula for Portland cement clinker was therefore



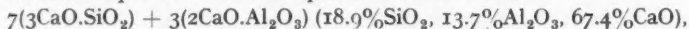
DUCHEZ<sup>26</sup> considered the principal constituent of Portland cement clinker was a solid solution of calcium oxide in dicalcium silicate of the general formula  $2.35\text{CaO} \cdot \text{SiO}_2$ .

REBUFFAT<sup>27</sup> showed that good quality Portland cement clinker contained no free calcium oxide. He failed to obtain tricalcium silicate and concluded that such a compound does not exist. Nevertheless, he considered that a composition approaching  $3\text{CaO} \cdot \text{SiO}_2$  was present as the chief constituent of Portland cement clinker but that this was probably an "indifferent combination" of calcium oxide with dicalcium silicate.

RICHARDSON<sup>10</sup> heated a homogeneous finely ground mix of  $3\text{CaO} + \text{SiO}_2$  for three hours at 1,650 to 1,700 deg. C. and obtained a snow-white, porous, and non-dusting product with optical properties very similar to Alite. He attempted to make the ternary compounds of  $\text{CaO}$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  (silico-aluminates of calcium) which earlier workers considered to be present in Portland cement clinker when insufficient calcium oxide to form entirely tribasic salts was present. He concluded from his experiments that no definite calcium silico-aluminate exists, but that this substance is a solid solution of mutually soluble silicates and aluminates. He next made several synthetic mixtures of the composition  $x(3\text{CaO} \cdot \text{SiO}_2) + y(3\text{CaO} \cdot \text{Al}_2\text{O}_3)$  where  $x$  and  $y$  varied. He found these burns were made up of Alite and Celite in varying proportions and concluded that these two substances were the main constituents of Portland cement clinker. In the more basic mixtures Celite decreases at the expense of Alite until at  $6(3\text{CaO} \cdot \text{SiO}_2)$  to  $1(3\text{CaO} \cdot \text{Al}_2\text{O}_3)$  the Celite vanishes. The product consists of only one constituent, Alite, and it is concluded therefore that Alite is a solid solution of the composition  $6(3\text{CaO} \cdot \text{SiO}_2) + 1(3\text{CaO} \cdot \text{Al}_2\text{O}_3)$ .

A mixture of the composition  $6(2\text{CaO} \cdot \text{SiO}_2) + 1(2\text{CaO} \cdot \text{Al}_2\text{O}_3)$  when burnt gave only one constituent identical with Celite, and Richardson concluded that Celite was a solid solution of the composition stated. Thus in clinkers (a) when sufficient calcium oxide is present only Alite occurs; (b) when less calcium oxide is present some Celite is present also; (c) the relative proportions of Alite and

Celite are dependent on (1) the basicity and (2) the ratio  $\text{SiO}_2 : \text{Al}_2\text{O}_3$ . When more alumina is present than corresponds with the formula

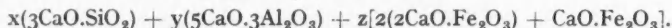


Richardson stated that the clinker departs from the usual Alite-Celite structure and a decided change occurs. A new solid solution of dicalcium silicate dissolved in dicalcium aluminate appears.

CAMPBELL<sup>28</sup> endeavoured to separate Celite (which is readily fusible) from the less fusible crystalline components by absorption in magnesia discs. Discs of well-burned clinker were placed between weighed discs of pure magnesia, and the temperature raised to clinkering point at which it was held for several hours. The material was allowed to cool slowly and the magnesia discs removed and analysed. Further discs were applied and the heating repeated until no further absorption took place. The material remaining was presumed to be Alite, and Campbell found that it amounted to 75 to 80 per cent. of the clinker. From the analyses of the Celite and Alite fractions and of the original clinker he came to the following conclusions: (1) The contention that Alite contains the bulk of the alumina and Celite contains all the iron is not sustained. The  $\text{Fe}_2\text{O}_3 : \text{Al}_2\text{O}_3$  molecular ratio is only a little higher in Celite than in Alite, and hence  $\text{Fe}_2\text{O}_3$  is molecularly equivalent to  $\text{Al}_2\text{O}_3$  so far as the formation of Celite is concerned. (2) Celite consists essentially of  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  and  $5\text{CaO} \cdot 3\text{Fe}_2\text{O}_3$  in which are dissolved  $2\text{CaO} \cdot \text{SiO}_2$  and  $\text{CaO}$ . (3) Alite consists of either  $\alpha$  or  $\beta$  dicalcium silicate holding calcium oxide in solid solution together with some aluminate and ferrite of the general formula  $5\text{CaO} \cdot 3\text{R}_2\text{O}_3$ . The concentration of the calcium oxide held in solution was thought to be dependent on the basicity of the mass and the temperature of burning, with the molecular ratio  $3\text{CaO}$  to  $1\text{SiO}_2$  representing the upper limit.

In synthetic fusions of Celites, Campbell found large well-developed crystals embedded in the solvent. By removing the solvent with magnesia discs he showed that these crystals consisted of tricalcium silicate. The solvent upon analysis corresponds almost exactly with the formula  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ , and in addition some dissolved  $2\text{CaO} \cdot \text{SiO}_2$  and  $\text{CaO}$ . Celites made in the same way, but with  $\text{R}_2\text{O}_3$  present almost entirely as ferric oxide, showed that the solvent consisted of  $5\text{CaO} \cdot 3\text{Fe}_2\text{O}_3$ . Following on the work of Sosman and Merwin on the calcium ferrites it was thought that the  $5\text{CaO} \cdot 3\text{Fe}_2\text{O}_3$  was a mixture of  $2(2\text{CaO} \cdot \text{Fe}_2\text{O}_3) + \text{CaO} \cdot \text{Fe}_2\text{O}_3$ .

A formula for cement was then given as follows:

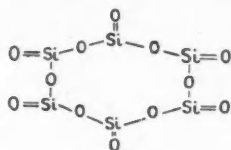


GLASENAPP<sup>29</sup> considered that the absorption of mother liquor by magnesia plates could not possibly be quantitative and therefore the chemical analyses were worthless. Campbell's "Alite" is probably a mixture of clinker forming materials with a residue of mother liquor.

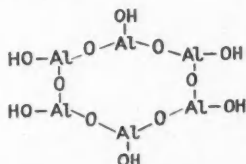
#### Hypothetical Structural Formula.

Asch and Asch<sup>30</sup>, whose work was chiefly speculative, believed that Portland cements are, theoretically, highly basic calcium salts of aluminosilicic acids,

i.e., basic salts of which the clays are the corresponding acids. They did not consider that Portland cement clinker contained a mixture of various silicates and aluminates. Each different Portland cement was regarded as a different calcium salt with a formula of its own. The authors discounted, on the grounds of polymorphism, the non-homogeneity of lime-alumina-silica melts as revealed by the microscope. If there was polymorphism, however, there should be a tendency to homogeneity by varying the physical conditions; this is not true of Portland cement clinker. By the use of their "hexite-pentite theory," Asch and Asch claimed to be able to give the structural formulæ of all Portland cements and naturally occurring silicates and aluminates. This theory was based on the following hypotheses: (1) 5 or 6 molecules of  $\text{SiO}_2$  or  $\text{Si}(\text{OH})_4$  combine to form either a pentagonal or hexagonal ring structure, e.g.



(2) alumina can behave in a somewhat similar manner:



(3) the theory assumed that all the natural and artificial silicates and aluminates form compounds which are combinations of numerous hexite and pentite linkings, condensations, etc.

Further structural formulæ have been offered by Martin<sup>31</sup> but all these constitutional formulæ are purely hypothetical. The hypothetical acids of Asch and Asch (6 to 24 replaceable hydrogen atoms, molecular weights 873 to 1,693) have no counterparts in nature. These formulæ do not take into consideration the possibility of impurities or slight inaccuracies in the analyses.

#### Application of the Phase Rule to Portland Cement Research.

As regards the preparation of synthetic compounds various methods have been employed, with the result that some disagreement has arisen as to the compounds formed by heating a particular mixture. The American school uses the "quenching method" in studying mixtures which have a slow melting process and are liable to undercooling (e.g., silicate mixes). The method is described by Shepherd and Rankin.<sup>32</sup> A small quantity of the material wrapped in thin platinum foil was held at a known constant temperature long enough for equilibrium to be reached, which might be a matter of hours, days, or even weeks. Then the charge was cooled (in such a manner as to freeze the equi-

brum) and examined by petrographic methods: if it was all glass, the temperature of heat treatment was above the liquidus; if it was a mixture of glass and crystals it was below the liquidus. By measuring the optical properties of the crystals they can be positively identified. With difficult mixtures it was customary to have two charges side by side, one initially glass the other previously crystallised. The heating must be continued long enough for both charges to attain the same condition. This method when applied to the constitution of Portland cement clinker was adversely criticised by those who considered that clinker is not in a state of equilibrium.

Ferguson and Merwin<sup>33</sup> described a type of furnace which was capable of maintaining, in an oxidising atmosphere, a charge at temperatures slightly above 1,700 deg. C. for several hours. The furnace was constructed on the cascade principle; the inner coil was of an alloy of platinum with 20 per cent. rhodium, the outer coil of pure platinum. The two coils were insulated from each other by well-burned magnesia powder and the inner coil was wound on a helically grooved magnesia tube. Field and Royster<sup>34</sup> described the methods of preparing synthetic melts. Details of an improved electric furnace and refinements in methods of measurement were given. The methods of synthetic investigation used by the Newberrys have been previously referred to.

(To be continued.)

#### REFERENCES.

- <sup>22</sup> Michaelis, *J. Prakt. Chem.*, 257 (1867); *J. Soc. Chem. Ind.*, 28, 836 (1909).  
<sup>24</sup> Zulkowsky, *Zeit. Chem. Ind.*, 290 (1901); *Stahl. u. Eisen*, 28, 690, 810.  
<sup>25</sup> Hendrickx, *Chim. et Ind.*, 8, 196 (1922).  
<sup>26</sup> Duchez, *Rock Products*, 1923, Vol. 26; Vol. 27 (1924); Vol. 28 (1925).  
<sup>27</sup> Rebuffat *Tonind. Ztg.* 117 1579.  
<sup>28</sup> Campbell, *J. Ind. & Eng. Chem.*, 5, 627 (1913). *J. Am. Chem. Soc.*, 24, 249 (1902); 24, 969 (1902); 26, 1143 (1904). *J. Ind. Eng. Chem.*, 6, 796 (1914); 9, 943 (1917); 7, 835 (1915); 11, 116 (1919). *Trans. Am. Cer. Soc.*, 17, 66 (1915).  
<sup>29</sup> Glasenapp, *Mitt. Zent. Ford. deut. Portland Zement Ind.*, 3, 21.  
<sup>30</sup> Asch and Asch, "The Silicates in Chem. and Commerce."  
<sup>31</sup> Martin, *Monit. Scient.*, p. 173 (1923), Vol. 13.  
<sup>32</sup> Shepherd and Rankin, *Am. J. Sci.*, 28, 308 (1909).  
<sup>33</sup> Ferguson and Merwin, *Am. J. Sci.*, 46, 417 (1918).  
<sup>34</sup> Field and Royster, *Tech. Paper*, No. 189, U.S. Bur. Stds.

### Book Review.

CIMENT SI TRASS. By A. STEPOE and H. TEODORU. Pp. 102. Bucharest: Institute of Industrial Chemistry.

THIS book is written in the Roumanian language, but it is accompanied by a summary in German which elucidates the numerous tables and graphs contained in the original. The subject dealt with is the alteration in the properties of trass by treatment with such reagents as hydrochloric acid, sulphuric acid, and caustic soda, and also by heating to temperatures up to 700 deg. C. The trass after treatment in these various ways was examined to reveal the changes in content of active silica; the setting-times, strengths, and other properties of mixtures of three types of Portland cement with the chemically altered trasses is fully recorded.

## Recent Patents Relating to Cement.

### Portland Cements.

No. 381,133. SMIDT & Co., Aktieselskab, F. L., 33, Vestergade, Copenhagen. May 25th, 1932.

A process for preparing nodules of raw cement consists in mixing at least one of the raw materials with an organic liquid and then adding water applied either directly or mixed with the other ingredient. The water drives off the organic liquid almost entirely. The organic liquid is such that it does not react chemically with the raw materials, is insoluble in water, and has a specific gravity different from that of water, e.g., crude oil, paraffin oil, or benzol. All the raw materials may be mixed with the organic liquid and water subsequently added, or one of the ingredients may be made into a slurry with the organic liquid and the other with water, the two slurries being then mixed. In an example clay and lime are ground together with an organic liquid and then, while the material is being stirred, water is added as a spray so that nodules are formed and the organic liquid is expelled. The material is then extruded by a press into a continuous length, which is cut up into suitable nodules. These may be dried by the waste gases from the kiln. In another example the clay is ground wet with all the water required in the finished nodules and the lime is ground with organic liquid. The two slurries are then mixed, with the result that the water expels the organic liquid almost entirely and nodules are formed. The material is then extruded as in the first example.

### Portland Cements.

No. 381,223. WHITE, H. E., 28, O'Connell Street, Sydney, Australia. July 2nd, 1931.

Portland cement is made by clinkering a mixture of precalcined calcareous material

## FOR SALE

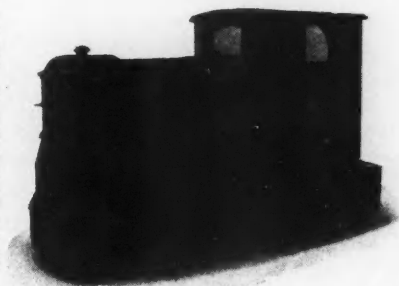
Estimated quantity of 4,000,000 tons of limestone lying on surface of about 140 acres, believed very suitable for cement manufacture. Full particulars and analysis given on application. Apply Box 840, Cement and Cement Manufacture, 20, Dartmouth Street, Westminster, S.W.1.

## PULLS LIKE— a steam loco

The Ruston Loco, fitted with a high efficiency Crude-Oil Engine, is built to pull and will do as much work as a petrol or paraffin loco of much greater rated B.H.P.

Users of Ruston Locos find that fuel bills have been reduced to such a degree that they are almost negligible.

If you would like to know more about the Ruston Loco fill in the coupon below.



## RUSTON & HORNSBY LTD LINCOLN

I am interested in  
CHEAP HAULAGE—

Name .....

Address .....

### Recent Patents Relating to Cement (Continued).

and ash obtained from heating furnaces burning powdered coal, and grinding the clinkers. When the calcareous material is limestone it may be calcined in the lump and then slaked to bring it to a fine dry powder, which is then mixed with the ashes, previously ground, or the lime may be mixed with water to form a slurry.

#### Cements.

No. 400,813. RIVERSIDE CEMENT CO., 621, South Hope Street, Los Angeles, U.S.A. January 27th, 1933. No. 2635.

A Portland cement of low heat of hardening comprises ground clinker containing less than 12 per cent. of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ , less than 3 per cent. of  $3\text{CaO} \cdot \text{Fe}_2\text{O}_3$ , at least 10 per cent. of  $3\text{CaO} \cdot \text{SiO}_2$ , and having a value less than 45 per cent. for the function per cent.  $3\text{CaO} \cdot \text{SiO}_2 + 2 \times$  per cent.  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ . The manufacturing steps and the type of raw materials are substantially the same as for ordinary Portland cements, but the raw materials are chosen to give different proportions of the four essential oxides: lime, silica, alumina and ferric oxide. In general the proportion of lime to silica is reduced and the proportion of iron oxide to alumina is relatively high but must not be substantially greater than one. The clinker is ground to normal cement fineness. In an example, a clinker comprises on analysis 63.1 per cent. of  $\text{CaO}$ , 2.5 per cent. of  $\text{MgO}$ , 25.9 per cent. of  $\text{SiO}_2$ , 3.5 per cent. of  $\text{Al}_2\text{O}_3$ , and 5 per cent. of  $\text{Fe}_2\text{O}_3$ . The constituent

compounds of this clinker are 29.4 per cent. of  $3\text{CaO} \cdot \text{SiO}_2$ , 52.1 per cent. of  $2\text{CaO} \cdot \text{SiO}_2$ , 15.2 per cent. of  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ , 0.8 per cent. of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ , and no  $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ . The  $\text{MgO}$  remains uncombined. The clinker is ground to a fineness corresponding to a specific surface of 1,450 sq. cms. per gram., and has a heat of hardening of 60.9 calories per gram.

#### Pozzolanic Cements.

No. 398,028. THORNTON, A. A., 7, Essex Street, Strand, London.—(Soc. Anon. Italiana per la Produzione Calci E. Cementi di Segni; 262, Corso Umberto I, Rome.) September 17th, 1932.

An hydraulic cement specially suitable for use in sea water is prepared by mixing calcium oxide with natural or artificial pozzolana and calcium sulphate in such proportions that the cement has an hydraulic index between 1 and 25. The cement is preferably in the form of a powder. The lime used should not contain more than 5 per cent. of impurities, and the calcium sulphate should be commercially pure. In an example 80 per cent. of natural pozzolana is mixed with 15 per cent. lime and 5 per cent. calcium sulphate, and gives a cement having an hydraulic index of 21.

#### RECENT PATENT APPLICATIONS.

No. 385,664.—G. O. CASE, E. M. ELLIS and L. H. MONTIGUE: Production of hydraulic cement.

D. R. E. WERNER, H. S. GIERTY and O. STALHAUE. No. 386,924.

## INDEX TO ADVERTISERS.

Avery, W. & T., Ltd. . . . .	—	Metropolitan-Vickers Electrical Co., Ltd. . . . .	x
Babcock & Wilcox, Ltd. . . . .	—	"Mieg" Mühlenbau und Industrie, A.-G. . . . .	vii
British Rema Manufacturing Co., Ltd. . . . .	—	New Conveyor Co., Ltd. . . . .	viii
British Thomson-Houston Co., Ltd. . . . .	—	Newell, Ernest, & Co., Ltd. . . . .	Front Cover
Brown, John, & Thos. Firth, Ltd. . . . .	ix	Pearson, E. J. & J., Ltd. . . . .	—
Davidson & Co., Ltd. . . . .	—	Polysius, G. . . . .	—
Davison, Charles, & Co., Ltd. . . . .	—	Richter, Oscar A. . . . .	—
Fellner & Ziegler . . . . .	v	Rolland, John, & Co. . . . .	—
Firth, Thos., & J. Brown, Ltd. . . . .	ix	Ross Patents, Ltd. . . . .	—
Frère, R., & F. Evrard . . . . .	viii	Ruston-Bucyrus, Ltd. . . . .	—
Gehr. Pfeiffer, Barbarossawerke A.-G. . . . .	vi	Ruston & Hornsby, Ltd. . . . .	59
General Electric Co., Ltd. . . . .	ix	Sock Machinery Co., Ltd. . . . .	vii
Glover, W. T., & Co., Ltd. . . . .	—	Smidth, F. L., & Co., Ltd. . . . .	ii, iii
Halipets, Ltd. . . . .	xii	Taylor, J. Daraley, & Co., Ltd. . . . .	v
Hepburn Conveyor Co. Ltd. . . . .	—	Union Des Bauxites . . . . .	vi
Klöckner-Werke . . . . .	xiii	Vickers-Armstrongs, Ltd. . . . .	xv
Krupp Grusonwerk . . . . .	—	Wye Foundry & Co., Ltd. . . . .	iv